

Effect of Landfill Leachate Organic Acids on Trace Metal Adsorption by Kaolinite

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Hexanoic (hex) and fulvic acid (FA), representing early and later stages of landfill leachate evolution, were examined for influence on trace metal adsorption by a poorly crystallized kaolinite (KGa-2). Our experiments represented a model approach to examine possible reaction mechanisms in an environmentally important ternary metal–ligand–mineral surface system. Batch experiments were conducted in 0.01 mol kg⁻¹ NaClO₄ at pH 3–8. Concentrations of metals (Cu, Cd, and Pb) and ligands were representative of those found typically in groundwater immediately down-gradient of a landfill. The presence of FA resulted in enhancement of metal adsorption below pH 5, whereas the presence of hex produced no significant net change in metal uptake. Measured surface charge properties of KGa-2 were combined with binary and ternary system data in constructing a quantitative model of the system. The simple combination of binary system results was not effective in predicting the observed ternary system behavior. In both ternary systems, the addition of ternary surface complexes (TSCs) to the models resulted in a satisfactory fit to the data. Our work suggests the strong possibility that TSC involvement in surface reactions of natural adsorbents may be a useful concept.

Introduction

Landfills are ubiquitous in modern society, and the proper management of their potential environmental impact is of the highest priority. Metals of environmental importance that are frequently present in leachate include Cd, Cr, Cu, Pb, Ni, Zn, and Hg (1). These pollutants may be mobilized by infiltrating rainwater to become part of the landfill leachate, a concentrated aqueous solution of refuse-derived materials. The leachate may then contaminate groundwater supplies by leakage through the landfill liner and/or the vadose zone. The composition of landfill leachate is, in part, time-dependent. Once formed, leachate evolves through a chemical “stabilization” process, involving several phases (2), the most important of which are herein referred to as the “acid” and “methane” phases.

In the acid phase, the organic fraction is dominated by volatile organic acids (VOAs), a collection of relatively low molecular mass aliphatic and aromatic carboxylic acids. Total organic carbon (TOC) concentration is at peak level in the life of the leachate, typically on the order of 20 g of C L⁻¹ (3,

4). During this phase, VOAs make up anywhere from 70 to over 95% of TOC (3, 5), and as a result, pH is typically between 4 and 5 (2), which is the pK_a range of the majority of VOAs (6). The remainder of the organic fraction is made up of phenols and trace amounts of neutral and basic compounds (5). The acid phase may last from less than 1 year to about 10 years, depending on site conditions (3). During the methane phase, microbial populations obtain energy from the breakdown of the VOAs and release methane as a respiratory byproduct. The TOC is generally much lower as a result (3), and pH rises to around 7. The organic fraction of the methane phase is dominated by more refractory compounds of high relative molecular mass, often described as similar to humic and fulvic acids (3, 7).

Given the significant TOC concentrations in both the acid and methane phases, metal–organic complexes are common in landfill leachate (4). Volatile organic acids may be important in the long-term migration of metals (8, 9). Humic and fulvic acids are known to be especially important complexers of metals in natural systems (10, 11), and the presence of similar compounds in leachate suggests a possible metal release mechanism. A major weakness in the ability to assess mobility of metals in leachate/soil systems is that few of the many possible metal complexes have been characterized (4).

The presence of inorganic or organic ligands may enhance, hinder, or have no effect on metal sorption, depending on the detailed chemical properties of the system (12, 13). If the ligand forms a stable complex in solution with the metal and this complex has no affinity for the sorbent surface, it will compete with the surface for the metal, likely hindering metal uptake. Alternatively, the complex may have a strong attraction for the surface, resulting in an increase in metal sorption through the formation of a ternary surface complex [TSC (14)]. The TSC may form by a surface bond to the ligand, metal, or a combination of both (13). A review of ternary system studies is provided in ref 15.

In this paper, a model adsorbent system is studied to evaluate the effects of representative acid and methane phase organic ligands on the attenuation of pollutant metals. The model system comprised kaolinite; the ligands hexanoic acid and aquatic fulvic acid (16); and the metals Cu, Cd, and Pb. The concentrations of ligands (200 mg of C L⁻¹ for hexanoic acid, 10 mg of C kg⁻¹ for fulvic acid) and of metals (100 µg L⁻¹ for Cu and Cd, 700 µg L⁻¹ for Pb) utilized in the model system reflect typical conditions in a contaminated aquifer immediately downgradient of a landfill (17–19). Quantitative modeling of the metal–ligand–kaolinite system was exploratory in nature, intended to illustrate ternary system behavior, not necessarily to duplicate realistic field conditions.

Materials and Methods

Metal–Kaolinite Systems. Stock suspensions of poorly crystallized Georgia kaolinite (KGa-2) were prepared as described by Schroth and Sposito (20). The background electrolyte was 0.01 M NaClO₄ (concentrations are expressed as *molality*, moles per kilogram of solution, *m*). Metal (M) stock solutions were prepared by dissolving M(ClO₄)₂ salts in 0.01 M NaClO₄, adjusted to pH 3 with HClO₄ and later diluted for sample preparation. Replicate pairs of batch samples were prepared at pH 3–8. For each sample, a mass of kaolinite suspension containing 350 mg of dry kaolinite was added to a 35-mL polycarbonate centrifuge tube. In numerical order, predetermined masses of (a) 0.01 M NaClO₄, (b) 0.01 M HClO₄ or NaOH, and (c) metal stock solution were added so that the total solution mass was 35 g and the KGa-2

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TABLE 1. Input Parameters and Model Results

		Concentrations of Components (<i>m</i>)			
(1)	[H ₂ CO ₃ *] ^a	1.00 × 10 ⁻⁵			
(2)	[XOH] _T ^b	3.59 × 10 ⁻⁴			
(3)	[YO ⁻] _T ^c	1.36 × 10 ⁻⁴			
(4)	[M] _T	1.57 × 10 ⁻⁶	(Cu), 8.90 × 10 ⁻⁷ (Cd), 3.38 × 10 ⁻⁶ (Pb)		
(5)	[L _a] _T ^d	5.01 × 10 ⁻⁵			
(6)	[L _b] _T ^d	1.90 × 10 ⁻⁶			
Conditional Stability Constants (<i>I</i> = 0.01 <i>m</i>)					
(a)	H ₂ O ⇌ H ⁺ + OH ⁻	log <i>K</i> _{OH} ^e	-14.0		
(b)	H ₂ CO ₃ * ⇌ H ⁺ + HCO ₃ ⁻	log <i>K</i> _{HCO₃} ^e	-6.3		
(c)	H ₂ CO ₃ * ⇌ 2H ⁺ + CO ₃ ²⁻	log <i>K</i> _{CO₃} ^e	-16.4		
(d)	XOH + H ⁺ ⇌ XO ₂ ⁺	log <i>K</i> ₁	3.5 ^{+0.2} _{-0.3}		
(e)	XOH ⇌ XO ⁻ + H ⁺	log <i>K</i> ₂	-7.2		
		Cu	Cd	Pb	
(f)	M ²⁺ + H ₂ O ⇌ MOH ⁺ + H ⁺	log <i>K</i> _{MOH⁺} ^e	-7.5	-7.6	
(g)	M ²⁺ + H ₂ CO ₃ * ⇌ MCO ₃ ⁰ + 2H ⁺	log <i>K</i> _{MCO₃} ^e	-10.0	-9.23	
(h)	M ²⁺ + 2H ₂ CO ₃ * ⇌ M(CO ₃) ₂ ²⁻ + 4H ⁺	log <i>K</i> _{M(CO₃)₂} ^e	-22.6		
(i)	XOH + M ²⁺ ⇌ XOM ⁺ + H ⁺	log <i>K</i> _X	-1.11 ^{+0.15} _{-0.15}	-1.45 ^{+0.13} _{-0.13}	-0.59 ^{+0.22} _{-0.23}
(j)	YO ⁻ + M ²⁺ ⇌ YOM ⁺	log <i>K</i> _Y	3.73 ^{+0.08} _{-0.08}	3.65 ^{+0.08} _{-0.09}	4.08 ^{+0.09} _{-0.09}
(k)	M ²⁺ + L _a ⁻ ⇌ ML _a ⁺	log β _{ML_a} ^d	3.90	3.51	4.29
(l)	M ²⁺ + HL _b ⇌ ML _b ⁺ + H ⁺	log β _{ML_b} ^d	1.494	1.34	1.64
(m)	XOH + M ²⁺ + HL _b ⇌ XOML _b ⁰ + 2H ⁺	log <i>K</i> _{XML_b} ^f	-0.01 ^{+0.42} _{-0.50}	-1.60 ^{+0.40} _{-0.29}	
(n)	XOH + M ²⁺ + L _a ⇌ XOML _a ⁰ + H ⁺	log <i>K</i> _{YML_a} ^f			3.47 ^{+0.36} _{-0.35}

Quadratic FA Adsorption Isotherm

$$\% \text{ FA adsorbed} = -1.26(\text{pH})^2 + 9.38(\text{pH}) + 58.29; r^2 = 0.87^{***}$$

^a [H₂CO₃*] = *P*_{CO₂} × *K*_{H,CO₂}; for a system open to the atmosphere, *P*_{CO₂} = 10^{-3.5} atm and Henry's law constant for CO₂ = 10^{-1.5} *m* atm⁻¹ (39).

^b Amphoteric site concentration estimated as 1 site nm⁻² (see text). ^c Permanent charge site concentration (20). ^d From Cabaniss and Shuman (23). Concentrations based on [FA]_T = 10 mg of C kg⁻¹. Stability constants for Cd and Pb were estimated from published complexation constant ratios with Cu (see text). ^e Value from the database in SOILCHEM (22), adjusted to *I* = 0.01 *m* using the Davies equation (40). No value indicates either a negligible species or no value reported. ^f Equation m did not provide an acceptable fit for Pb data, and eq n was not usable for Cu and Cd data.

solids concentration was approximately 10 g kg⁻¹. Above pH 6, a preequilibrated mixture of NaClO₄ and NaOH was added in place of a and b above. A kaolinite-free blank solution was prepared with each sample replicate to check for loss of metal to the container walls.

The samples and blanks were equilibrated at 23 ± 1 °C by slow rotation for 15 ± 1 h while open to the atmosphere and then centrifuged at 27 000 RCF for 20 min. Portions of the supernatant solution (SS) and blank were analyzed for H⁺ concentration (-log [H⁺] values are hereafter reported as pH) using an Orion model 8102BN combination pH electrode (20). All solutions were analyzed for metal concentration by inductively coupled argon plasma spectroscopy (ICP, Perkin-Elmer Model P-40).

Ligand-Kaolinite System. Adsorption of Suwannee River fulvic acid [FA (16)] onto KGa-2 at 23 ± 1 °C was quantitated by solution TOC analysis. Samples and blanks were prepared in 35-mL centrifuge tubes in the same manner as with the metal-kaolinite system, with a sample total FA concentration of 18.7 mg kg⁻¹, equivalent to 10 mg of C L⁻¹ (16). Preequilibrated stock solutions at pH 6.5–8 were made with FA to avoid significant pH changes during sample preparation. Samples were equilibrated, centrifuged, and stored in the same manner as the metal samples. Total organic carbon in the SS was measured by persulfate oxidation on a Dohrmann model DC-80 carbon analyzer. Percent FA adsorption was calculated from the difference between initial and final FA concentrations. This same procedure was followed in studies of hexanoic acid (hex) adsorption at an initial concentration of 200 mg of C kg⁻¹.

Ternary System. Metal-FA-kaolinite samples were prepared and analyzed in the same manner as in the metal-kaolinite and FA-kaolinite systems. The total concentration of each component was the same as that reported for the

binary systems. There was no particular order of addition of metal and FA standards during sample preparation, since changing the order produced no significant difference in metal uptake (data not shown).

Modeling. The program FITEQL (21) was used to calculate conditional stability constants for solution-surface equilibria with the nonelectrostatic option selected. Relevant data on carbonate and hydroxide equilibria were incorporated from the speciation program SOILCHEM (22). The Cu-FA complexation model of Cabaniss and Shuman (23) also was incorporated, as described below.

The pH dependence of amphoteric sites on KGa-2 was quantitatively modeled as a basis for metal and ternary surface complex modeling. Net proton surface charge data for KGa-2 (20) were interpreted in a manner analogous to that for aqueous species equilibrium (24). Surface site reactions were modeled as in eqs d and e in Table 1, where the amphoteric surface site XOH may be either SiOH or AlOH. The total concentration of XOH in solution was incorporated into FITEQL on the basis of an assumed site density. Reported surface site densities of kaolinite vary between 0.6 (13) and 6 sites nm⁻² (25). A value of 1 site nm⁻² was assumed, but also varied as part of a sensitivity analysis. The values of log *K*₁ and log *K*₂ were constrained by the measured point of zero net proton charge [pznpc = 5.36 ± 0.02 (20)]. Sensitivity was evaluated by adjusting the best-fit value of log *K*₁ or log *K*₂ until the model deviation from any single data point had been made to exceed 0.15 pH unit, above which was considered an unacceptable fit.

With log *K*₁ and log *K*₂ fixed, the metal-kaolinite system data were modeled using average amphoteric (XOH) and permanent charge (YO⁻) surface sites (eqs i and j in Table 1), a commonly used approach to metal adsorption (e.g., refs 26 and 27) that has received support from spectroscopic

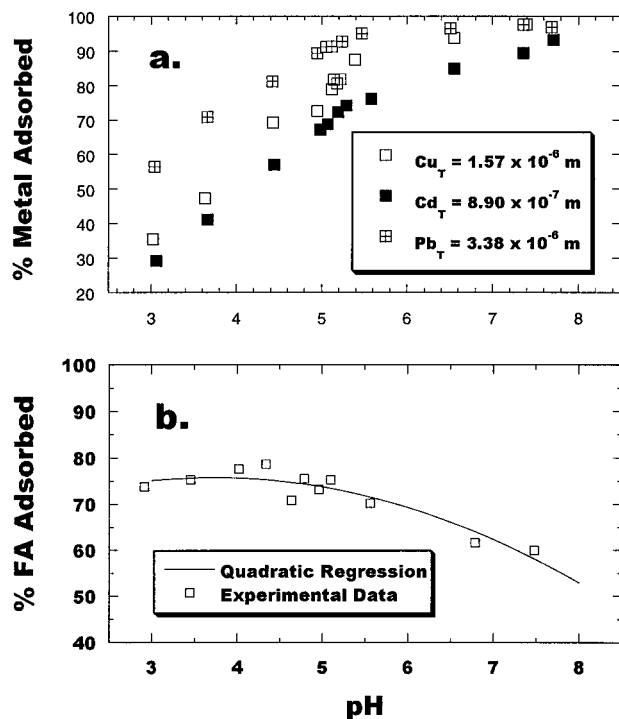


FIGURE 1. (a) Adsorption of Cu, Cd, and Pb to kaolinite KGa-2 as a function of pH. (b) Adsorption of 18.7 mg kg^{-1} fulvic acid by kaolinite KGa-2. Line represents a quadratic least-squares fit to the data. $[\text{KGa-2}] = 10 \text{ g kg}^{-1}$; $I = 0.01 \text{ M NaClO}_4$.

studies (28, 29). The total concentration of permanent charge sites, $\{[\text{YO}]_T$, the negative of the permanent structural charge density, σ_0) was $13.6 \text{ mmol kg}^{-1}$ dry kaolinite (20). For sensitivity analysis, an acceptable fit was defined as a log K value producing less than 5% metal adsorption difference from any single data point.

The Cu–Suwannee River FA complexation model of Cabaniss and Shuman (23), developed for the same FA and for metal and FA concentration ranges that encompass those in the present study, was used in modeling the metal–FA–kaolinite system. These authors stated that use of the model outside its calibrated pH range (5–8.5) will likely involve some error. Maximum error in the present study was therefore expected at pH 3–5. Although the FA was modeled with five discrete categories of noninteracting metal binding sites (23), we found that the first two site categories, L_a and L_b , dominated metal complex speciation for the conditions of our experiments, thus permitting all of our simulations to be performed with site categories L_a and L_b only.

The Cu binding constants of the Cabaniss and Shuman (23) model were scaled for Cd and Pb to account for differences in binding strength. The ratios of complexation constants for Cu, Cd, and Pb in FA complexes thus were assigned values of 1.0, 0.9, and 1.1, respectively (Table 1), on the basis of ratios of published constants for organic acids and NOM (6, 30).

Results

Binary Systems. Results of the metal adsorption experiments are presented as adsorption edges in Figure 1a. Metal loss from blank solutions was less than 10%, with the notable exception of Pb above pH 7. In these cases, Pb loss correlated very closely to the percentage precipitation of PbCO_3 predicted by SOILCHEM (22), and Pb was nearly 100% adsorbed by kaolinite, so the loss observed in the blank was assumed not to affect the interpretation of results. With the exception of one replicate pair in the Cu data, all replicate

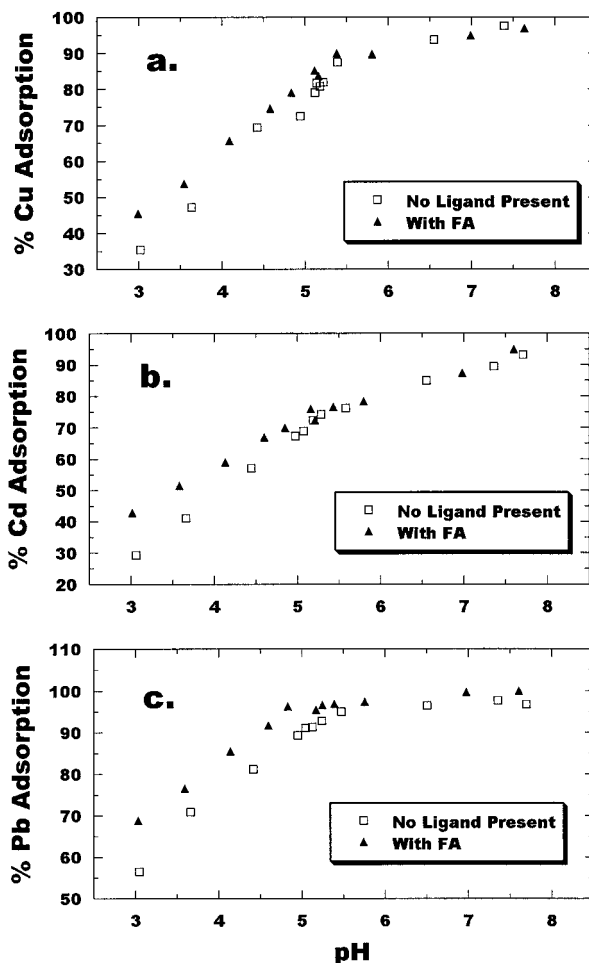


FIGURE 2. Adsorption of Cu, Cd, and Pb by kaolinite KGa-2 in the presence of 18.7 mg kg^{-1} fulvic acid. $[\text{KGa-2}] = 10 \text{ g kg}^{-1}$; $I = 0.01 \text{ M NaClO}_4$.

percent adsorption values agreed within 2%. The value of pH_{50} [the pH value at which 50% of the metal is adsorbed (13)] increased in the order $\text{Pb} < \text{Cu} < \text{Cd}$, which also describes the order of decreasing relative affinity for the kaolinite surface, in agreement with similar studies in the literature on different adsorbents (e.g., ref 31).

Results of the FA adsorption experiments are presented as an adsorption envelope in Figure 1b. About 75% of the added FA was adsorbed throughout the pH range of our experiments, with a modest decrease at $\text{pH} > \text{pznpc}$. These results are consistent with published studies of NOM adsorption (32, 33). There was no significant hex adsorption by KGa-2 throughout the pH range investigated (data not shown; see ref 15). Because FA adsorption was nearly independent of pH (Figure 1b) and the adsorption mechanism of FA on kaolinite is likely more than simple complexation, the use of optimized surface complexation constants to describe the adsorption data did not seem warranted. A simple quadratic regression curve was constructed through the data (Figure 1b), and this equation (Table 1) was used to calculate the adsorbed fraction of FA at each pH value for the ternary system data. The standard error of the % FA estimate (S_{y-x}) was 2.44%.

Ternary System. The effect of FA on the adsorption of Cu, Cd, and Pb is illustrated in Figure 2. There was an average enhancement of metal adsorption between 7.7 and 11.7% for $\text{pH} < 4.9$ and no more than 4.1% for $\text{pH} \geq 4.9$. Adsorption of the three metals in the presence of $200 \text{ mg of C kg}^{-1}$ was essentially the same as that with no hex present (Supporting Information; see ref 15).

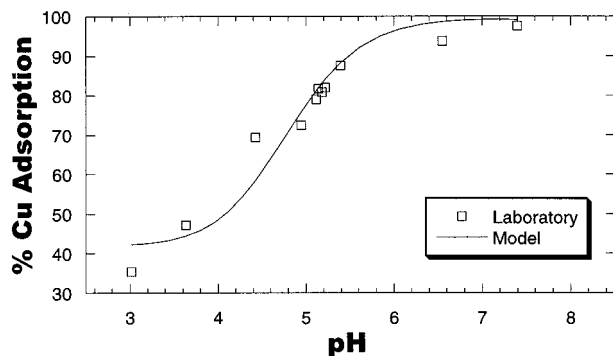


FIGURE 3. Two-site model approximation for Cu adsorption data. Line represents the "best fit" (defined in the text) to the data after adjusting the values of $\log K_X$ and $\log K_Y$. Model parameter values are provided in Table 1 {components 1–4 and eqs a–j}.

Modeling

Kaolinite Surface Charge. Model parameters incorporated into FITEQL (21) for the determination of pH-dependent surface charge were components 1 and 2 and eqs a–e in Table 1. No sensitivity to $\log K_2$ was observed because the experimental pH range (3–5.5) was well below pK_2 . The variation in $\log K_1$ corresponding to the range in reported kaolinite site densities, described above, is approximately 2.6 (for 6 sites nm^{-2}) to 3.9 (for 0.6 sites nm^{-2}). It is evident that site density is a sensitive parameter.

Metal–Kaolinite Systems. The metal–kaolinite binary system was modeled with components 1–4 and eqs a–j in Table 1. The fit for the Cu system is illustrated as an example in Figure 3. The values of $\log K_X$ and $\log K_Y$ for each metal (Table 1) reflect the relative affinity sequence implied in Figure 1a.

Ternary Systems. A simple combination of binary system model components drastically underpredicted Cu adsorption (Figure 4a), evidently because of complexation of Cu by FA in solution. Uncertainty in the model parameter values alone could not explain the large discrepancy between the model and observed data. To account reasonably for this discrepancy, TSC formation was added to the simulations. At low pH, some additional metal adsorption may result in the form of a ligand-bridged TSC, since the organic ligands are at maximum adsorption density. This conceptual model has been proposed in several other ternary system studies (e.g., refs 33 and 34). The ligand-bridged TSC model used in our study involved two assumptions: (1) the fraction of FA–metal complex that is adsorbed is equal to the adsorbed fraction of total FA predicted by the quadratic isotherm (Table 1), and (2) none of the L_x ($x = a, b$) metal binding sites is quantitatively linked to FA adsorption, so that all L_x sites are available for metal binding. Assumption 2 is justified by the fact that, if one assumes even 100% metal complexation (an impossibly high percentage), no more than 6.5% of the combined ($L_a + L_b$) sites is occupied by a metal under our experimental conditions. The percentage of total metal adsorbed at a given pH (% M_{ads}) may therefore be calculated as

$$\%M_{\text{ads}} = \{ \% \text{FA}_{\text{ads}} / 100 \} \{ \sum (\% \text{ML}_x) \} + \{ \sum (\% \text{M-kaol}) \} \quad (1)$$

where % FA_{ads} is the percent FA adsorbed as calculated by the quadratic isotherm, $\sum (\% \text{ML}_x)$ is the sum of the concentrations of FA–metal complexes as a percentage of total metal concentration, and $\sum (\% \text{M-kaol})$ is the sum of the concentrations of XOM^+ and YOM^+ surface complexes as a percentage of total metal concentration (Table 1). No optimization of constants was performed in FITEQL since

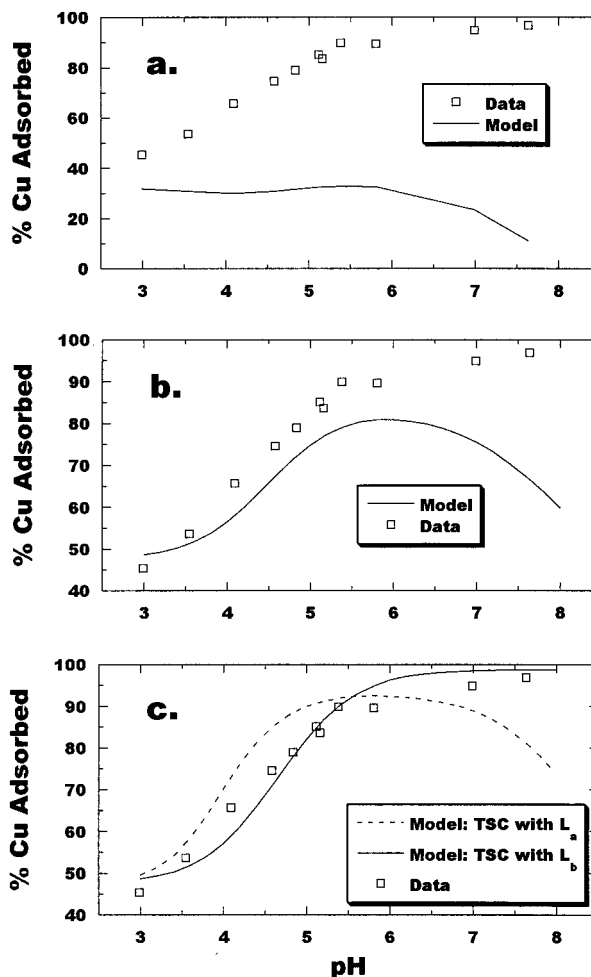


FIGURE 4. (a) Two-site model approximation for Cu adsorption data in the presence of 18.7 mg kg^{-1} FA. The model includes components 1–6, eqs a–l, and the FA adsorption isotherm in Table 1. (b) Model from panel a with ligand-bridged TSC added (eq 1). (c) Model from panel b with cation-bridged TSC added (eq m).

all input parameters were taken either from binary system models (Table 1) or from published values (23). Figure 4b shows the predicted Cu adsorption compared to our experimental data. Even with over 60% of the Cu complex adsorbed, the model still predicts far less Cu uptake than was observed at high pH. Copper speciation was dominated by FA complexes in this pH range.

The existence of both ligand- and cation-bridged TSCs has been supported spectroscopically in ternary metal–ligand–adsorbent systems (35, 36). A cation-bridged TSC was added to the model in the form of either eq m or eq n in Table 1. The best-fit results are shown for Cu in Figure 4c. The model was not sensitive to the value of a $\log K$ for a TSC at permanent charge sites (Y). This site was thus eliminated and only amphoteric sites (X) were used in the cation-bridged TSC model. A cation-bridged TSC was also used successfully in the hex modeling experiments (Supporting Information; see ref 15), where binary model equilibria also did not predict ternary system data.

The concept of TSC formation in trace metal–FA systems is not shared by all researchers. Murphy and Zachara (37) observed enhanced metal uptake at low pH *only* for humic acid (HA), which they found to be more strongly bound to the adsorbent surface than FA. Lo et al. (31) observed either no effect or decreased adsorption of Cd onto landfill soil samples in the presence of HA, depending on the HA concentration. Neal and Sposito (38) found that Cd adsorp-

tion on several soils was decreased by the application of sewage sludge and was increased by removing organic matter from soils. Overall, observations of ligand effects on metal adsorption appear to be highly dependent upon experimental conditions, especially the relative concentrations of reacting components (15).

There are several assumptions concerning the reactions in our ternary system model; however, all assumptions made were consistent with previous studies of less complex systems. Our primary purpose was to describe reasonable mechanisms and to take advantage of recently measured kaolinite surface charge properties (20). More realistic experimental conditions, such as greater P_{CO_2} or competitive effects of other cations, were beyond the scope of the present study. It was important to us to produce a good fit to the data while minimizing the number of adjustable parameters by fixing those for the binary systems before adding more complexity. To this end, the goals of our model approach were met. As Figure 4 shows clearly, if the TSC concept was not considered, a significantly reduced metal adsorption (and hence greater metal mobility) would be predicted for neutral and slightly alkaline conditions. Though the overall effects of FA and hex on metal adsorption may appear to be modest or absent, our analysis suggests there is a large effect on adsorption through the formation of TSCs.

Most importantly, our results suggest that successful prediction of complex system behavior cannot be achieved simply from a combination of results from simpler systems. This perspective has significance for the use of geochemical models that utilize single-component or binary system databases. Our data and modeling exercise suggest the strong possibility that TSC involvement in the surface reactions of natural adsorbents may be a useful concept.

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Supporting Information Available

Text, references, one table, and two figures plus their captions giving further data and input parameters and model results for the metal/hexanoic acid/kaolinite system (6 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$16.50 for photocopy (\$18.50 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL <http://www.chemcenter.org>. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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